Growth of Germanium Nanowires on Silicon(111) Substrates by Molecular Beam Epitaxy

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Abstract:

Heteroepitaxial growth of Ge nanowires was carried out on Si(111) substrates by MBE. Au seeds were used as precursor for the VLS growth of the nanowires. Even if the Au droplets do not act as catalyst for the dissociation of gas, they are local preferential areas where the energetic barrier of Ge nucleation is lowered compare to the remaining non activated surface. Two sets of Au seeds were used as precursors for the VLS process. The first set have an average diameter of 125 nm and the second of 25 nm. In-situ RHEED monitoring showed a Au wetting layer between these seeds before the nanowires growth as well as at the end of the Ge nanowires growth. It means that the wetting layer acted as a surfactant from the Si(111) surface to the Ge grown layer between the nanowires. Analysis of SEM images brought the fact that the diffusion of gold from the droplets on the surface and the sidewalls of the nanowires via the Ostwald ripening is a key parameter of the growth of the nanowires.

Keywords: nanowires, germanium, MBE, VLS

Introduction:

One dimensional structures such as nanowires (NWs) have been a focus of considerable research interest because of their emerging quantum properties, potential applications in electronic and sensors and for the miniaturization of devices.[1] A renewed interest is focused on germanium due to several key points: its higher hole carrier mobility compared to silicon, its smaller bandgap which is suitable for some detectors or solar cells and its capacity to create a ferromagnetic alloy with manganese which leads to the integration of magnetic materials into the already setted semiconductors technology for the so-called spintronic.[2-4] In most cases, NWs are grown by using chemical vapor deposition (CVD) via the vapor-liquid-solid (VLS) mechanism as first described by Wagner and Ellis in the early 60's.[5] In its classical concept small metal seeds like gold droplets are formed on the surface of a substrate. When the precursor gases of the CVD technics reach the seeds, they act as catalysts and molecules are dissociated. Semiconductor atoms are thus incorporated into the liquid metal droplets where a supersaturation occurs. Semiconductor atoms precipitate at the liquid-solid interface and the wires grow with the same diameter as the metal droplets. In the case of the molecular beam epitaxy (MBE) technique, the metal droplets do not act as catalyst to crack the precursor molecules since in MBE processes impinging species are already atomic. According to this the layer between the droplets and the wires should grow at the same speed. However wires grow faster than the layer as described by Schubert & al.[6] Several models have been built to explain the growth of whiskers by MBE.[7,8] The growth of whiskers by MBE implies a gradient of the chemical potential between an impinging atom on the substrate surface and an impinging atom at the top of the wire, a contribution of the Gibbs-Thomson effect and a contribution of the diffusion on the substrate surface and on the whisker side wall surface.

There are few works reporting the growth of NWs by physical vapor deposition (PVD) even if this is a good method for an accurate control of the growth conditions.[9] In this article we will describe the heteroepitaxial growth of Ge NWs on silicon substrate by MBE.

Experiments:

(111) oriented Si wafers were used as substrates. They were chemically cleaned according to the conventional Shiraki process before being introduced in the MBE chamber. RHEED (Reflection high-energy electron diffraction) pattern showed a 1x1 reconstruction of the Si surface. The MBE growth experiments were carried out in UHV characterized by a base pressure of about $5x10^{-10}$ mbar. Two Knudsen effusion cells

were available for these experiments: Ge and Au. Temperature was measured by a thermocouple situated between the heater and the back of the sample holder. Previous calibrations have led to an estimated uncertainty of ±20°C. We performed some flash annealing up to 900°C until we obtained the 7x7 reconstruction to be sure that the surface was cleaned. Thin films of gold were then deposited on the Si substrates to form the metal droplets at room temperature. We have produced two batches of samples. On the first one a 3.5 nm thick Au thin film was heated to 400°C to produce Au seeds with an average diameter of 125 nm by dewetting of the initial film. On the second batch a 2 nm thick Au film was heated to 340°C to create Au seeds with an average diameter of 25 nm. During the following 120 min of Ge deposit to grow the NWs, the Ge flux was kept constant to 1.1 Å/s and the substrate temperature was 300°C. Beforehand the flux was calibrated using RHEED oscillations during a Ge deposit on Ge(111) surface. Samples were investigated in-situ by RHEED (electron beam energy: 30kV, STAIB Instrumente) and ex-situ by a JEOL JSM-6320F SEM (Scanning Electron Microscope).

Results and discussion:

The germanium NWs were grown by MBE on Si(111) substrates from gold seeds using the so-called VLS process. The Au droplets define activated areas where the chemical reactivity differ from the remaining substrate surface: the energy barrier for the nucleation of germanium is lowered. As the environment is UHV, this remaining surface is clean and free of any oxide layer. The VLS process in a MBE system differs slightly from the known VLS process in CVD by the fact that the Au droplets do not catalyze the cracking of the precursor molecules. The enhanced growth rate of the NWs is thus mainly related to diffusion processes taking place on the substrate surface and the NW side walls.

a) Gold droplets and wetting layer:

The use of gold as seeds for the Ge NWs is based on the occurrence of an Au-Ge eutectic point on the Au-Ge phase diagram at relatively low temperature. The bulk eutectic point is T_e=361°C. However growth below the eutectic temperature have been reported.[10]

Size and density of gold beads depend on the thickness of the precursor thin film and on the substrate temperature. The first batch (set 1) of gold droplets illustrated on the SEM image of fig.1a came from a thin film of 3.5 nm and a substrate annealing temperature of 400°C. The average diameter of the beads is 125 nm and the density reported (tab.1) is 8×10^8 cm^{-2}. The dispersion is quite low around 15%. RHEED in-situ monitoring did not present any spots which could have been attributed to the three dimensional gold beads maybe because of the electrons beam absorption by these beads. However RHEED patterns displayed 1/3 and 2/3 stalks in the [11-2] directions (fig.1.c). It is characteristic of the $\sqrt{3} \times \sqrt{3}$ structure of a two dimensional continuous gold wetting layer in between the droplets. The second set (set 2) of Au seeds was created from a 2 nm thick film with a substrate annealing temperature of 340°C. SEM images (fig.1d) and the histogram extracted from these images (fig.1e) show that the average diameter is 25 nm and the density of seeds is 2.5×10^{10} cm^{-2} (tab.1). Droplets are thus smaller than in the first set and the diameter dispersion is higher (35%). AFM images (fig.1.f) taken on the second set of droplets displayed a preferential nucleation of the seeds on the step bunches of the Si(111) surface as already mentioned.[11] For lower substrate temperatures (under 320°C) the dewetting of the gold thin film is uncompleted and the density of seeds is very low.

b) Germanium NWs growth:

Using the two previous sets of droplets, germanium nanowires were grown at a substrate temperature of 300°C. Generally speaking, we observed on the surface two kind of three dimensional structures: NWs that had a preferential (110) orientation and presented a smooth or step by step decrease of their diameters (fig 2.a and 2.b) and rather big misshapen structures. The SEM backscattered electrons image (fig.3.a) clearly show the brighter germanium layer grown on the non activated part of the Si(111) substrate and the droplets at the top of the whiskers. The thickness of the germanium layer is about h_s=490 nm. The nominal amount of deposited Ge with the effusion cell was h=720 nm. Figure 3b is a secondary electrons SEM image taken on a cleaved sample. It illustrates the fact that NWs keep their shape when they are covered by the grown layer. It means that the maximum quantity $(h-h_s)/h$ of Ge atoms available for the growth of the NWs is only 30% of impinging germanium. The growth ratio defines by "length of the NWs over the grown layer"/h_s was estimated to 0.70 ± 0.09 in the case of the set 1 and to 0.73 ± 0.12 in the case of set 2. In both cases the values are estimated by a statistic calculus from the whole available SEM images. These values are close to the one reported by Werner & al,[12] and suggest that the growth of whiskers from smaller seeds is faster. Diffusion process of Ge ad-atoms on the surface substrate and along the side walls of the growing whiskers is the main Ge supplier for the droplets rather than the direct impinging atoms. NWs growth by MBE is mainly controlled by the ad-atoms diffusion.[6,7,13,14] Regarding the density of the NWs, we found an average density of 0.6×10^8 cm^{-2} for the set 1 and 4×10^8 cm^{-2} for the set 2 (tab.1). The ratios R_1 and R_2 of NWs on initial droplets are 7.5% for the set 1 and 0.6% for the set 2 and the ratio "droplets Ø25/Ø125" (R_3) and "NW Ø25/Ø125" (R_4) are respectively 31 and 6.6. It seems that the growth from larger Au seeds is preferential. However the whiskers we observed in the case of set 2 have a diameter higher than the average value 25 nm as shown in fig. 2a: the diameter decrease from 70 nm to 43 nm between the two white markers. These can be explain by the Ostwald ripening of the gold droplets during the germanium deposit as already reported.[12,15] Whiskers with small diameter did not grown during enough time because of the ripening and vanishing of their gold droplet and were then buried into the Ge layer. On the contrary wires with bigger gold seeds kept a droplet at their top during the whole germanium deposit time even if this diameter decreased. The diffusion of gold can contribute significantly to the growth of the observed misshapen structures.

In-situ RHEED monitoring of the Ge deposit was carried out on the two sets of samples. Results (fig. 4) were the same regardless of the set. The RHEED pattern show the [1-10] and [11-2] directions of a Ge surface with a lot of three dimensional diffraction spots. These spots are attributed to the diffraction of the electron beam by the misshapen structures and the NWs and appear on the diffraction stalks and out. Spots on the diffraction stalks can be related to the electrons diffraction by the structures epitaxialy grown normal to the substrate surface. Spots out of the stalks are attributed to the diffraction by the structures epitaxialy grown along the (110) direction since the diffraction plans will be tilted according the growth direction. The spots appeared as soon as the mask of the Ge effusion cell was opened meaning that the growth of the 3D structures started at once. On the [11-2] we clearly observed the typical $\sqrt{3}x\sqrt{3}$ structure of a gold wetting layer. The Au layer acted as a surfactant from the Si(111) surface to the terminal Ge layer. Basically during the whole Ge deposit time, Ge ad-atoms always impinged and diffused on a Au rich layer.

Conclusion:

Ge NWs were grown on a Si(111) surface by MBE using the VLS process. Gold droplets were used as metal seeds. Two type of Gold beads were produced by dewetting of Au thin films deposited with an effusion cell. The first type of beads is characterized by an average diameter of 125 nm and a second type by an average diameter of 25 nm. In-situ RHEED monitoring showed the presence of a remaining Au wetting layer between the Au droplets. Then Ge NWs were grown from the two types of samples. Irrespective of these two sets, RHEED patterns presented typical spots of a 3D surface and revealed that there was still a Au wetting layer. SEM images displayed surfaces with 3D misshapen structures and with NWs. Analyses of the SEM images showed that the observed wires from the 25 nm seeds set had a diameter equal or bigger than 100 nm and are longer than the wires grown from the 100 nm seeds set. These observations suggest that the Ostwald ripening of droplets and the diffusion of gold onto the surface and side walls of NWs is a key parameter of the MBE growth of the NWs.

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Table:

Density /cm²	droplets	NW	Ratio NW/droplets
Set 2: 25 nm	$2.5x10^{10}$	$4x10^{8}$	R_1=0.6%
Set 1: 125 nm	$8x10^{8}$	$0.6x10^{8}$	R_2=7.5%
Ratio 25/125	R_3=31	R_4=6.6	

Table 1: densities of the gold droplets and of the Ge NWs subsequently grown .

Figures:

1. a) SEM image of gold droplets corresponding to a gold deposit of 3.5 nm and a substrate temperature of 400°C. b) Histogram showing the diameter versus the number of the seeds for image a. The solid line is an eye-guide for a gaussian distribution. c) RHEED pattern ([11-2] direction) of the Si(111) surface covered by 125nm diameter gold droplets. No signature of the droplet is visible. 1/3 and 2/3 stalks are characteristics of the $\sqrt{3}x\sqrt{3}$ structure of a two dimensional continuous gold wetting layer in between the droplets. d) SEM image of gold droplets corresponding to a gold deposit of 2 nm and a substrate temperature of 340°C. e) Histogram showing the diameter versus the number of the seeds for image d. f) AFM image of gold droplets (set2, average 25nm) on Si(111) surface.
2. NWs (set 2) showing a smooth (a) and step by step (b) decrease of their diameter.
3. a) Cross-section SEM backscattered electrons image of a Si(111) substrate with grown Ge layer and whiskers. b) Cross-section SEM secondary electrons image of a cleaved sample. Inside the white circle there is a wire going through the deposited Ge layer.
4. RHEED patterns along the [1-10] and [11-2] directions taken at the end of the Ge deposit time.

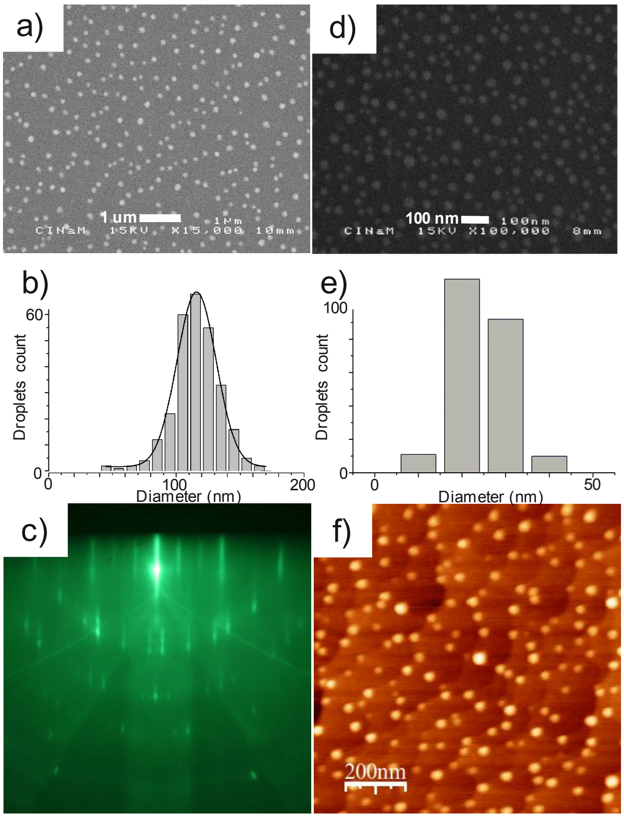
a)
1 um
CIN≡M 15KV X15,000 10mm
d)
100 nm
100nm
CIN≡M 15KV X100,000 8mm
b)
Droplets count
60
0
0
100
200
Diameter (nm)
e)
Droplets count
100
0
0
50
Diameter (nm)
c)
f)
200nm

Figure 1

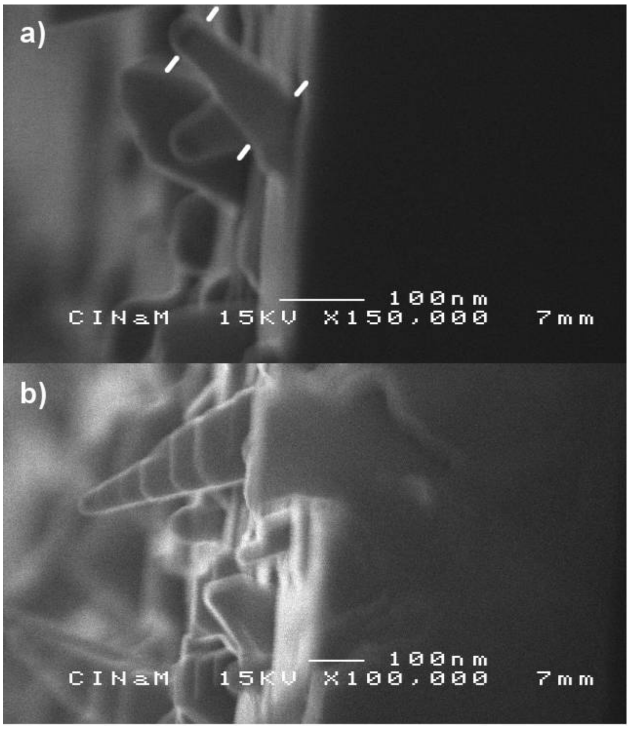
a)
100nm
CINaM 15KV X150,000 7mm
b)
100nm
CINaM 15KV X100,000 7mm

Figure 2

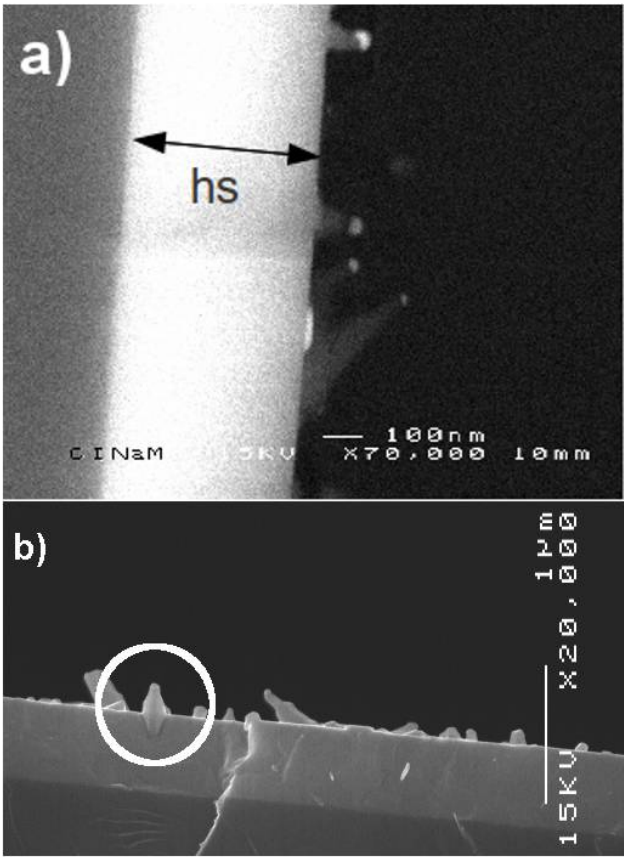

Figure 3

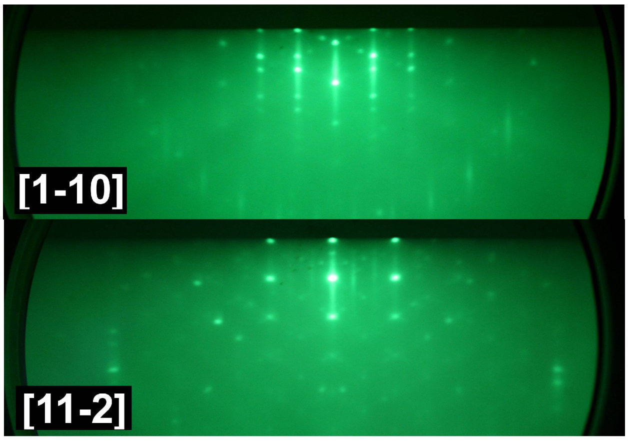

Figure 4